

IV.J DMFC and SOFC

IV.J.1 Direct Methanol Fuel Cells

Piotr Zelenay (Primary Contact), Eric Brosha, John Davey, Fernando Garzon, Christine Hamon, Yu Seung Kim, Manoj Neergat, Piotr Piela, Bryan Pivovar, Geraldine Purdy, John Ramsey, John Rowley, and Mahlon Wilson

Materials Science and Technology Division

Los Alamos National Laboratory

Los Alamos, New Mexico 97545

Phone: (505) 667-0197; Fax: (505) 665-4292; E-mail: zelenay@lanl.gov

DOE Technology Development Manager: Nancy L. Garland

Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

Objectives

The main research objective is to develop materials, cell components and optimize operating conditions of direct methanol fuel cells for maximum power density and fuel conversion efficiency at a minimum cost. Individual objectives include:

- Design and optimize membrane-electrode assemblies for enhanced cell performance.
- Advance electrocatalysts for methanol oxidation and oxygen reduction to increase power density and lower total precious metal loading.
- Characterize and optimize non-Nafion[®] polymers with reduced crossover and improved performance.
- Model, design and demonstrate advanced cell components.
- Identify main routes of cell performance degradation and improve cell (stack) durability.
- Collaborate with industry on efficient system integration and technology transfer to facilitate expedient commercialization of direct methanol fuel cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- D. Fuel cell power system benchmarking
- O. Stack material and manufacturing cost
- P. Durability
- Q. Electrode performance
- R. Thermal and water management

Approach

- Build, operate and test electrochemical cells and fuel cells with advanced materials such as anode and cathode catalysts, membranes, and membrane-electrode assemblies (MEAs).
- Develop, through experimentation, thorough understanding of the key factors impacting cell performance and performance durability.

- Maximize efficiency, power and energy density of DMFCs by creative design of stack components and experimental verification of the hardware performance.

Accomplishments

Durability

- Determined impact of Ru crossover on DMFC cathode performance
- Proposed two methods for Ru crossover reduction
- Quantified anode & cathode surface area losses in the 850-hour life test
- Correlated transformation of Pt oxide and cathode performance loss
- Demonstrated new Nafion[®]-based MEA with performance loss reduced to ~12% over 3000 hours

Membrane & MEA Research

- Demonstrated much higher selectivity of 6F-CN-35 membrane in operating cell than Nafion[®]
- Maintained superior performance of the 6F-CN-35 MEA for 700 hours

Cathode Electrocatalysis

- Synthesized Pt and Pt-Co catalysts (unsupported and supported) with average particle size reduced by more than 40%

High Specific-Power Portable Stack

- Designed, built, and successfully tested first short six-cell stacks

Future Directions

Remainder of FY 2004

- Determine and optimize performance of new LANL-synthesized highly-dispersed cathode catalysts
- Verify performance stability of novel Nafion[®]-based MEAs, recently life-tested for 3000 hours
- Demonstrate a complete 25-cell high specific-power stack for portable applications

FY 2005 Objectives (All key to successful commercialization of DMFCs)

- Determine impact of changing hydrophilic/hydrophobic properties of the cathode on DMFC performance and performance durability
- Explore introduction of non-precious metal electrocatalysts as means of lowering DMFC cost
- Minimize, or eliminate Ru crossover in DMFCs
- Establish materials and techniques allowing consistent fabrication of highly selective and durable alternative MEAs for DMFCs

Introduction

DMFC research at Los Alamos National Laboratory has focused on developing materials and designing optimum operating conditions for direct methanol fuel cells for portable power devices (*e.g.*, commercial electronics, battery replacement for the military) and transportation (*e.g.*, on-board auxiliary power units). The main objective of the DMFC research has been to demonstrate that methanol-

based systems can meet performance (power-density, energy-conversion efficiency, durability) and cost targets.

Approach and Results

In FY 2004, our effort in electrocatalysis has concentrated on developing Pt and Pt-Co cathode catalysts with significantly reduced average particle size to: (i) improve cathode performance *via* better

catalyst utilization; and (ii) lower Pt catalyst cost by reducing required loading. Platinum black catalysts have been synthesized in-house by treating $\text{Na}_6[\text{Pt}(\text{SO}_3)_4]$ with hydrogen peroxide at 80°C , followed by reduction of Pt oxides with formic acid (HCOOH). In one approach, Pt black catalyst was precipitated directly from the solution, while in the other it was first deposited on silica. As shown by XRD patterns in Figure 1a, the average particle size of in-house fabricated Pt black and Pt/SiO₂ catalysts, has been measured at 3.8 nm and 4.8 nm, respectively, which represents significant particle size reduction relative to the state of the art Johnson Matthey Pt black catalyst for DMFC cathodes (Hi-SPEC™ 1000, ~ 6 nm average particle size). DMFC performance of both LANL catalysts was found to be the same as that measured with the reference Johnson Matthey catalyst (Figure 1b). It is expected that further purification of the in-house prepared catalysts and optimization of the membranes specifically for the new catalysts will result in their improved performance over the reference material.

Another approach to improving cathode electrocatalysis has been through in-house low- and high-temperature synthesis of the binary Pt-Co catalyst. So far, the high-temperature method has led to a carbon-supported Pt-Co catalyst with a very high content of the metal (60 wt%) and small average particle size (6.2 nm). Much smaller (2.7 nm) particle size of unsupported Pt-Co catalyst has been achieved *via* the low-temperature method. The two Pt-Co catalysts will be further optimized and DMFC-tested in the near future.

A year ago, we developed alternative membrane-electrode assemblies to standard Nafion® that for the first time promised considerable performance improvement. That research, carried out in close collaboration with Virginia Polytechnic Institute, led to the demonstration of two new polymers from the poly(arylene ether sulfone) family: 6F and 6F-CN. This year, we have developed membrane-electrode assemblies that use the best performing alternative membrane (6F-CN-35) with Nafion®-based electrode formulations. These MEAs exhibit good and stable DMFC performance, and no increase in high-frequency resistance over long times of operation, which

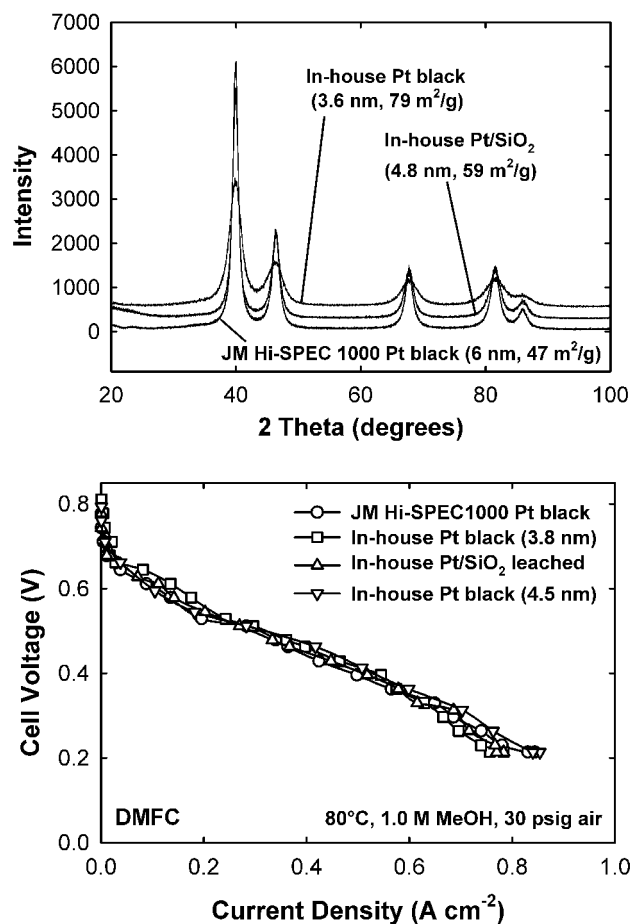


Figure 1. (a) XRD patterns for in-house fabricated Pt catalysts and the reference Pt black catalyst; (b) DMFC polarization plots for three in-house fabricated Pt catalysts and the reference catalyst (Hi-SPEC™ 1000).

suggest a robust interface between 6F-CN-35 membrane and Nafion®-based electrodes (Figure 2). Although the percent performance loss in a 700-hour life-test shown in Figure 2 is similar for the alternative and Nafion® MEAs, the performance advantage of the 6F-CN-35 membrane is due its higher selectivity that is maintained throughout the entire life test. This result represents a significant achievement in the process of making alternative membranes practically viable for large-scale DMFC use.

In parallel with the fundamental research in catalysis, membranes, and MEAs, which has remained the focal point of the direct methanol fuel cell program at LANL, we achieved substantial

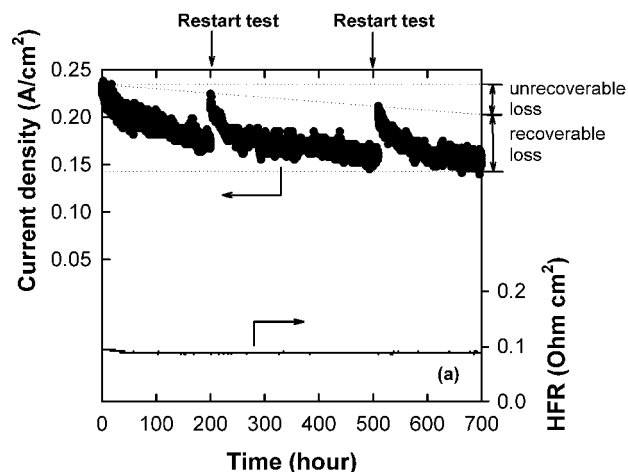


Figure 2. 700-hour DMFC life test of a 6F-CN-35 membrane with Nafion®-based electrodes; cell voltage 0.5 V, cell temperature 80°C.

progress in the design of a high specific-power DMFC stack for portable power applications (effort currently supported internally by Los Alamos National Laboratory under technology maturation initiative). First tests of short six-cell stacks confirmed very good performance of the new hardware in general, and at very low reagent flows in particular. When completed later in FY 2004, the 25-cell stack, weighing slightly more than 200 g, is expected to generate specific power of between 400 and 500 W/kg. Also, at the final stage of the DARPA-sponsored Palm-Power project, we manufactured four stack prototypes that, together with LANL-built methanol concentration sensors, were integrated by our partner, Ball Aerospace & Technologies Corporation, into two complete 20 W system prototypes for the military (Figure 3). The systems are capable of operating with 33% fuel conversion efficiency at the design power point (20 W).

FY2004 marks further advancements in DMFC durability research at Los Alamos. Based on the data acquired in an experimental setup for parallel durability testing of several MEAs the following main routes in of the DMFC performance degradation were identified: (i) surface area loss of the anode and the cathode, (ii) cathode surface oxidation, (iii) diminished cathode hydrophobicity (flooding), and (iv) ruthenium crossover and subsequent accumulation at the cathode. We found a

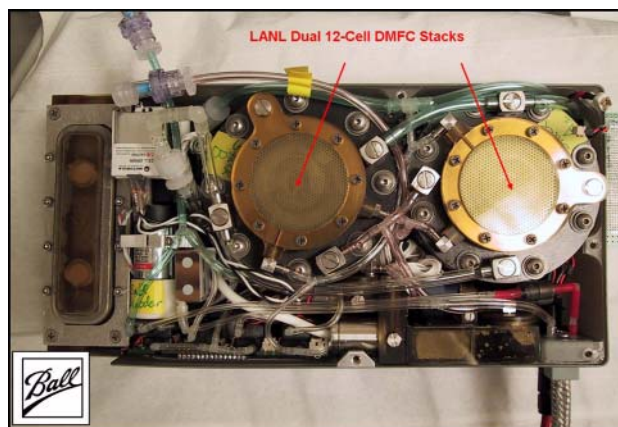


Figure 3. 20-W DMFC system for portable power application integrated by Ball Aerospace & Technologies Corporation, using two round stacks and methanol concentration developed and built at LANL (system cover removed).

35%-40% loss in the active surface area of the anode over 850 hours of cell operation. Such loss appears to have relatively limited impact on the anode performance in methanol oxidation; a result that is likely to be caused by high initial loading of the Pt-Ru anodes used in testing (*ca.* 8 mg cm⁻²). The impact of a similar percent-loss in the active surface of the cathode (up to 40%) has been more difficult to assess because of a number of factors impacting the long-term performance of the cathode. The effect of surface area on the cathode performance will be the subject of an in-depth study in the near future.

As reported earlier, most of the short-term DMFC performance loss is caused by the surface oxidation of the platinum catalyst at its operating potential of 0.80-0.85 V. Recent experiments reveal that cell performance loss over the first ten hours of operation can be correlated with an increase in the coverage by surface oxide (hydroxide) only in the first two hours of cell operation. At time longer than two hours, a steady drop in the cathode's oxygen reduction reaction (ORR) activity can be correlated with a gradual transition of the oxide layer (Figure 4). That transition is believed to lead to a change in the electronic properties of the catalyst, most likely caused by a slow inversion of the platinum and oxygen atoms on the catalyst surface.

Ruthenium crossover is another source of non-recoverable loss in DMFC performance, which was

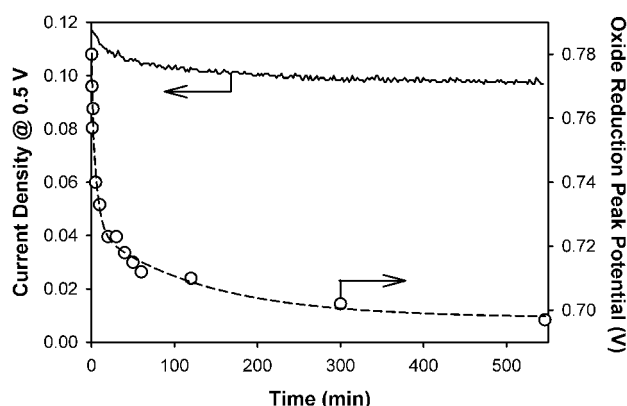


Figure 4. Correlation between cell performance loss at 80°C (left axis) and gradual change in the properties of the surface Pt oxide, as indicated by negative shift in the peak potential of oxide reduction under voltammetric conditions (right axis).

first demonstrated at LANL in FY2003 with a carbon monoxide surface probe technique. This year's research has focused on the effect of ruthenium crossover on the oxygen reduction reaction in an operating cell. A typical cell performance loss observed with Los Alamos DMFC MEAs (Nafion® 117 membrane, Pt-Ru black anode, Pt black cathode) after constant-voltage operation for several hundred hours at 70–80°C is ~40 mV at a cell current density of 100 mA cm⁻² (Figure 5a). This performance loss represents a combined effect of the lowered activity of Pt cathode in ORR and its reduced tolerance to crossover methanol, both effects caused by the deposition of Ru on the surface of platinum catalyst. The most extreme contamination of the cathode catalyst, e.g. caused by prolonged cell “reversal”, can lead to much greater performance penalty, which may approach as much as 200 mV at the reference current density of 100 mA cm⁻². In such cases, cell performance closely resembles that of a cell operating with a Pt-Ru black cathode instead of a Pt black cathode (Figure 5b).

Conclusions

The main conclusions from the DMFC research performed at LANL in the past year can be summarized as follows:

- Techniques for the preparation of unsupported Pt black and Pt-Co black catalysts as well as

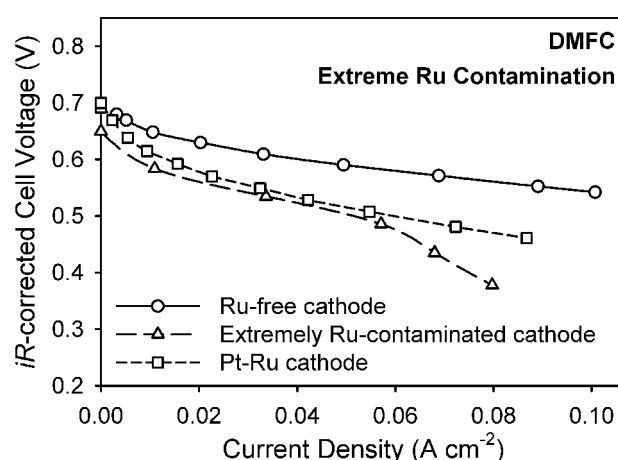
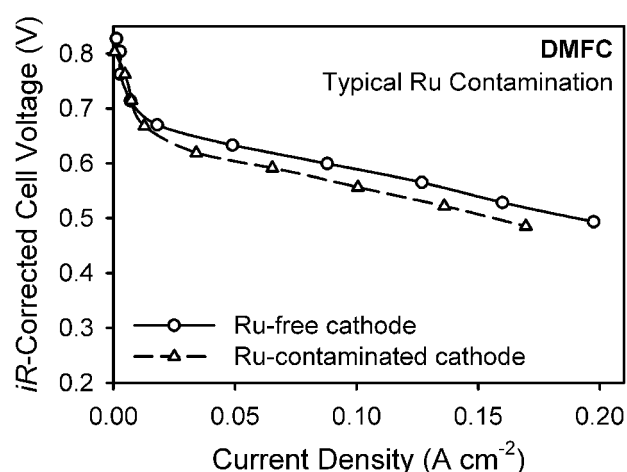


Figure 5. Performance penalty induced by the deposition of crossover Ru after (a) hundreds of hours of cell operation under “typical” DMFC conditions and (b) prolonged operation under extreme conditions in a fuel cell stack (possible cell “reversal”); performance of the cell with a Pt-Ru cathode shown for reference in (b).

carbon-supported Pt-Co with high metal-to-carbon ratio which lead to substantial (up to 55%) reduction in the average particle size of DMFC cathode catalysts are available. While recently obtained catalyst formulations still need purification and optimization before being used in well-performing MEAs, highly-dispersed Pt black catalysts, synthesized *via* the direct and the silica routes, have already matched performance of the best commercial cathode catalysts.

- Modifications to the interface between the 6F-CN-35 membrane and Nafion®-based

catalyst layers give rise to stable and well performing membrane-electrode assemblies capable of outperforming Nafion[®]-based MEAs in a 700-hour life test.

- Thanks to the implementation of a high-temperature processing step, significant improvement in the performance durability of a Nafion[®]-based MEA has been demonstrated in a 3000-hour test, with the performance drop over that time reduced to *ca.* 40%.
- Good short-stack performance of the new LANL hardware promises very high (up to 500 W/kg) specific power of the next generation DMFC stacks for active portable power systems.
- Performance loss of the cathode caused by the oxide (hydroxide) formation is caused by the drop in active sites for oxygen reduction and by the change in the electronic properties of the catalysts due to slow reorganization of the surface oxide.
- Ruthenium crossover in cells with Nafion[®] membranes leads to the contamination of Pt sites by Ru with resulting drop in cathode performance. The performance penalty under operating conditions of an efficient DMFC (high voltage operation) has been measured at 40 mV, with lowered activity of the cathode in ORR and impaired ability of the Pt catalyst to handle methanol crossover contributing to the observed performance loss.

FY 2004 Publications

1. "Processing induced morphological development in hydrated sulfonated poly(arylene ether sulfone) copolymer membranes" Y.S. Kim, L.M. Dong, M.A. Hickner, B.S. Pivovar, and J.E. McGrath, *Polymer*, **44** (19), 2004, 5729-5736.
2. "A Six-Cell 'Single-Cell' Stack for Stack Diagnostics and Membrane Electrode Assembly Evaluation," B. Pivovar, F. Le Scornet, C. Eickes, C. Zawodzinski, G. Purdy, M. Wilson, and P. Zelenay, in *Proton Conducting Membrane Fuel Cells III*, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
3. "The Effect of BPSH Post Treatment on DMFC Performance and Properties," M. Hickner, Y. Kim, J. McGrath, P. Zelenay and B. Pivovar, in *Proton Conducting Membrane Fuel Cells III*, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
4. "Optimization of Carbon-Supported Platinum Cathode Catalysts for DMFC Operation," Y. Zhu, E. Brosha and P. Zelenay, in *Proton Conducting Membrane Fuel Cells III*, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
5. "Electrochemical and XRD Characterization of Pt-Ru Blacks for DMFC Anodes," C. Eickes, E. Brosha, F. Garzon, G. Purdy, P. Zelenay, T. Morita and D. Thompsett, in *Proton Conducting Membrane Fuel Cells III*, T. F. Fuller, S. Gottesfeld, M. Murthy, and J. W. Van Zee (Eds.), ECS Proceedings, Electrochemical Society, Pennington, New Jersey, in press.
6. "Direct Methanol Fuel Cell Performance of Disulfonated Poly (Arylene Ether Benzonitrile) Copolymers," Y.S. Kim, M.J. Sumner, W.L. Harrison, J.S. Riffle, J.E. McGrath, B.S. Pivovar, *J. Electrochem. Soc.*, in press.
7. "Ruthenium Crossover in the Direct Methanol Fuel Cell with a Pt-Ru Anode," P. Piela, C. Eickes, E. Brosha, F. Garzon and P. Zelenay, *J. Electrochem. Soc.*, in press.
8. "New Proton Exchange Membranes (PEM) for Direct Methanol Fuel Cells (DMFC)," M. A. Hickner, Y. S. Kim, F. Wang, W. Harrison, M. Hill, L. Dong, B. Pivovar, P. Zelenay and J. E. McGrath, *Electrochim. Acta*, in press.

FY 2004 Presentations

1. Materials Science and Technology Division Review, Los Alamos National Laboratory, Los Alamos, New Mexico, May 27 – 29, 2003. Title: "Direct Methanol Fuel Cells for Portable Power: A Tangible Step Towards Fuel Cell

- Commercialization” J. R. Davey, C. Eickes, R. E. Fields, D. M. Lopez, P. M. Piela, B. S. Pivovar, G. M. Purdy, J. C. Ramsey, J. Rowley, M. S. Wilson, Y. Zhu, and P. Zelenay* (**invited lecture**).
2. 5th Gordon Research Conference on Fuel Cells, Bristol, Rhode Island, July 27 – August 1, 2003. Title: “AC Impedance Diagnostics of DMFC Stacks” P. Piela*, R. Fields and P. Zelenay.
 3. 204th Meeting of the Electrochemical Society, Orlando, Florida, October 12 – 17, 2003. Title: “Ruthenium Crossover in the DMFC with a Pt-Ru Black Anode”; P. Piela, C. Eickes and P. Zelenay*.
 4. 204th Meeting of the Electrochemical Society, Orlando, Florida, October 12 – 17, 2003. Title: “AC Impedance Diagnostics of DMFC Stacks” P. Piela*, R. Fields and P. Zelenay.
 5. 204th Meeting of the Electrochemical Society, Orlando, Florida, October 12 – 17, 2003. Title: “An Impact of Cathode Operating Conditions on DMFC Performance”; Y. Zhu and P. Zelenay*.
 6. Military Fuel Cells Conference, Washington, D.C., October 20-21, 2003. Title: “PEM Fuel Cell R&D at Los Alamos National Laboratory” B. Pivovar* and P. Zelenay (**invited lecture**).
 7. 2003 Fuel Cell Seminar, Miami Beach, Florida, November 3 – 6, 2003. Title: “AC Impedance Diagnostics of DMFC Stacks” P. Piela*, R. Fields and P. Zelenay.
 8. 2003 Fuel Cell Seminar, Miami Beach, Florida, November 3 – 6, 2003. Title: “Direct Methanol Fuel Cell Research at Los Alamos: From Fundamentals to Stack Prototyping” P. Zelenay (**plenary lecture**).
 9. Tactical Power Sources 2004, Arlington, Virginia, January 28 – 30, 2004. Title: “Current State of the Art and Future Research Needs for the Development of DMFC” P. Zelenay (**invited lecture**).
 10. Military Fuel Cells Conference, Las Vegas, Nevada, October 20 – 21, 2003. Title: “Direct Methanol Fuel Cell Research at Los Alamos National Laboratory” P. Zelenay (**invited lecture**).
 11. Small Fuel Cells 2004, The Knowledge Foundation’s 6th International Symposium, Arlington, Virginia, May 5 – 7, 2004. Title: “Direct Methanol Fuel Cells for Portable Power: Promises and Potential Limitations” P. Zelenay (**invited plenary lecture**).
 12. International Energy Agency Annex XVI Meeting, Newcastle upon Tyne, United Kingdom, May 6-7, 2004. Title: “Ruthenium Crossover in the Direct Methanol Fuel Cell with a Pt-Ru Black Anode” Piotr Zelenay (delivered by Debbie Myers).
 13. 205th Meeting of the Electrochemical Society, San Antonio, Texas, May 9 – 13, 2004. Title: “Development of Cathode Catalysts for DMFCs” M. Neergat* and P. Zelenay.
 14. 205th Meeting of the Electrochemical Society, San Antonio, Texas, May 9 – 13, 2004. Title: “Non-Platinum Electrocatalysts for Polymer Electrolyte Fuel Cells: Fuel Cell Evaluation of Oxygen Reduction Catalyst” S. Levendosky, P. Atanassov*, J. Davey and P. Zelenay.
 15. 205th Meeting of the Electrochemical Society, San Antonio, Texas, May 9 – 13, 2004. Title: “Design Aspects of DMFC Stacks at Los Alamos National Laboratory” J. C. Ramsey*, D. Lopez, P. Zelenay and M. S. Wilson.
 16. 205th Meeting of the Electrochemical Society, San Antonio, Texas, May 9 – 13, 2004. Title: “Performance Durability Issues in DMFC Operation” P. Piela, M. Neergat and P. Zelenay*.

Special Recognitions & Awards

1. Los Alamos National Laboratory Distinguished Performance Award – *September 2003*
2. Los Alamos National Laboratory Patent & Licensing Award – *February 2004*
3. R&D 100 Award (nominee) – *March 2004*

Patent Issued

1. “Catalyst Inks and Method of Application for Direct Methanol Fuel Cells” – *United States Patent No. 6,696,382 B1, issued Feb. 24, 2004*